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Synthesis, Characterization, and Sensitivity Analysis of Urea Nitrate (UN)

by William M Sherrill

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Weapons and Materials Research Directorate

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14. ABSTRACT Urea nitrate (UN) was synthesized and analyzed to determine the rate of mass loss of the material at various temperatures. The sensitivity of the material to external impact was also determined. From the results of the study, UN is safe to store under normal operating conditions.				
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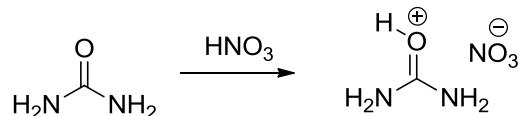
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1. Introduction

Urea nitrate (UN) is a high explosive obtained from the combination of urea and nitric acid (HNO_3). Due to its simple composition, ease of manufacture, and higher detonation parameters than ammonium nitrate, it has become one of the explosives of choice among terrorist organizations.¹⁻⁴ UN is readily formed by treating a solution of urea in water with concentrated nitric acid. The resulting salt precipitates out of solution and is easily recovered by simple filtration. Care must be taken to keep the salt free of moisture as even traces of moisture cause the breakdown of the material into its parent components, urea and HNO_3 . This is one of the reasons that post-detonation detection of UN is extremely difficult.⁴

Scheme1. Synthetic route to UN



2. Thermal Stability Studies

A 25-gram (g) sample of UN was prepared according to literature methods and analyzed for purity using a variety of analytical techniques.⁵ In order to verify sample purity, differential scanning calorimetry (DSC) was employed to determine the sample's melting and decomposition point (see Fig. 1). Literature values for the melting point vary from a low of 152 °C with decomposition to 162 °C.^{6,7} The sample synthesized melted at 161.5 °C going straight into decomposition with a peak decomposition temperature of 165.5 °C. This is within the literature range, and the DSC trace matches closely with the one published by Oxley.⁵

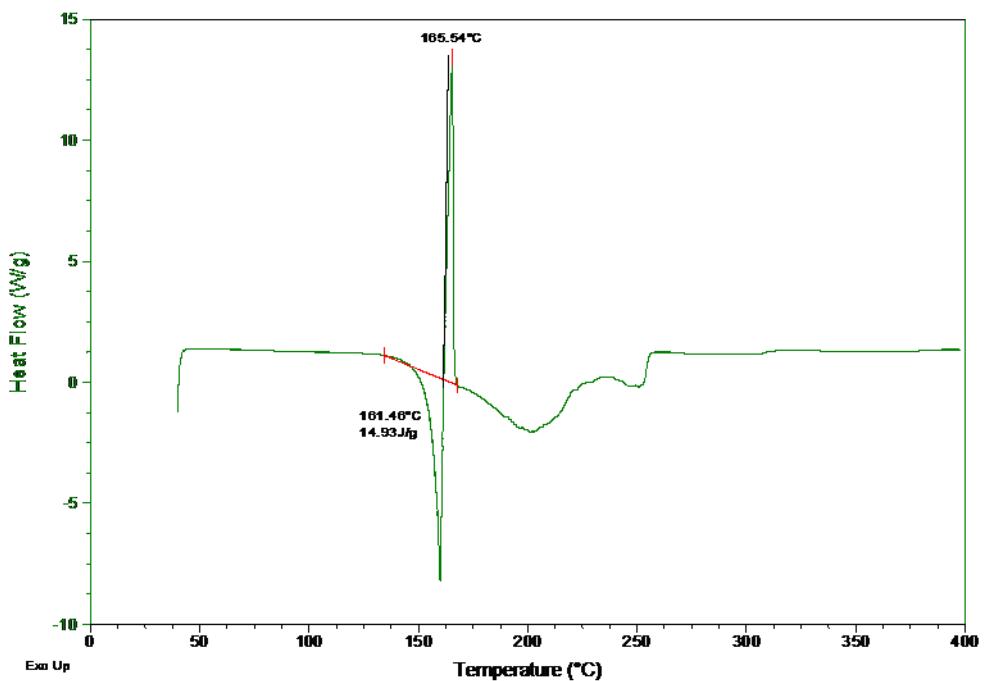


Fig. 1 DSC trace of UN

Thermogravimetric analyses (TGA) were conducted at various temperatures to determine what would be the optimum temperature to conduct vacuum thermal stability evaluations as well as for potential magazine storage concerns. Initial samples were run at 80 and 90 °C to verify the urea nitrate sample synthesized exhibited a similar trend in mass loss to published literature.⁸ We were pleased to find that the sample synthesized when subjected to those temperatures for 500-min lost mass in a similar fashion to what was published in Oxley's paper. Once it was established that the materials were exhibiting reasonable mass loss, isothermal experiments were conducted at temperatures ranging from 40 to 90 °C (Fig. 2). Two samples covered with a standard DSC pan lid with a pinhole in it were also run at 60 and 80 °C to evaluate the effect of covering the samples (Fig. 3).

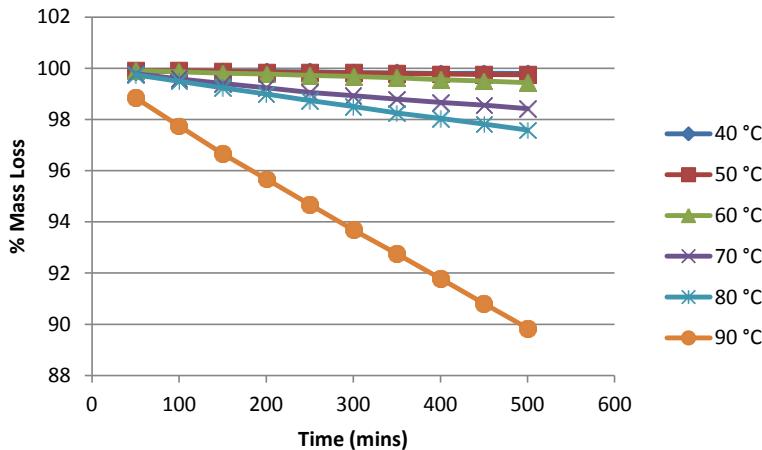


Fig. 2 Isothermal mass loss at various temperatures of uncovered pans

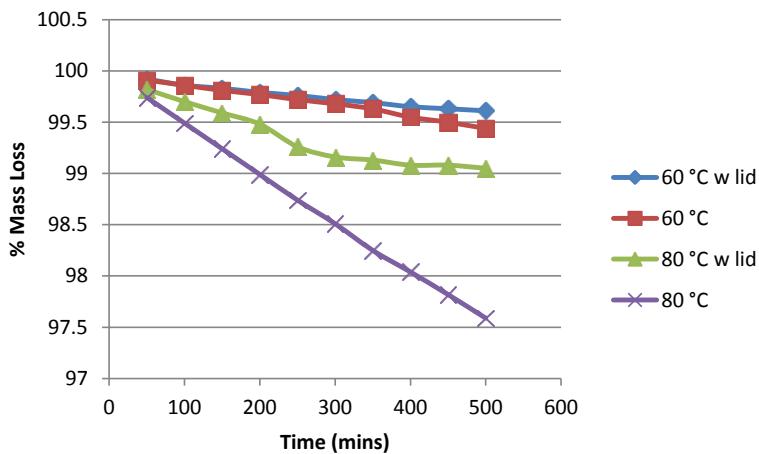


Fig. 3 Comparison of mass loss in covered pinhole vs. uncovered pans

As expected, there was a marked decrease in the amount of mass lost as a function of temperature. This is the same trend that was observed at the higher temperatures in Oxley's paper.⁵

3. Rate of Mass Loss Determination

The plots in Figs. 2 and 3 show that the rate of mass loss of the material resemble the change in concentration of zero order reaction over time. Using the rate law for zero order reaction kinetics, the slope of the line is the rate of the reaction for the corresponding temperature. The equations for the zero order reaction and half-life equation follow.

Eq. 1 shows the zero order reaction kinetics rate law (k is rate constant; $[A]$ is the concentration of UN)

$$\text{Rate} = k[A]^n. \quad (1)$$

Eq. 2 shows the half-life ($t_{1/2}$) equation for a zero order reaction ($[A]_0$ is the concentration at time 0)

$$t_{1/2} = \frac{[A]_0}{2k}. \quad (2)$$

The following Table shows the rates of mass loss and half-life at various temperatures.

Table Rates of mass loss and half-life at various temperatures

Temp (°C)	Sample Mass (mg) ^a	Rate (% loss/min) ^b	$t_{1/2}^c$ (min)
40	4.813	0.0002	250,000
50	4.826	0.0004	125,000
60	4.977	0.0010	50,000
70	4.747	0.0030	16,667
80	5.351	0.0048	10,417
90	4.838	0.0198	2,525
60 covered	5.123	0.0007	71,429
80 covered	4.867	0.0018	27,778

^amilligram; ^bpercent mass loss per minute; ^chalf-life.

With all of the samples starting at 100% mass as the $[A]_0$, the units for the rate constant of the reaction become expressed in percent mass loss per minute instead of the more traditional moles per second and it is possible to then calculate the half-life in minutes of the reaction using Eq. 2.

4. Experimental

4.1 General Considerations

Infrared (IR) spectra were recorded on a Bruker Alpha-T equipped with a platinum ATR diamond cell (DC) and were sampled neat. DSC was obtained on a TA instruments Q10 or Q20 calorimeter using standard aluminum pans with a pinhole lid. All solvents and reagents were procured from commercial sources and used without further purification unless noted. TGA was conducted on a TA instruments TGA Q50 with nitrogen as the purge gas. The pans used were standard DSC aluminum pans and unless noted were run uncovered. For the samples that were run covered, the pans were covered with standard DSC lids with a pinhole to allow any evolved gasses to escape. The initial sample sizes for all runs were 5.0 ± 0.4 mg.

Note: Urea nitrate can be explosive if handled improperly when dry. Although no incidents resulted from the synthesis and analysis of this material, proper care, expertise, and equipment should be utilized whenever handling any potentially energetic materials.

4.2 Synthesis

Urea (21.72 g \times millimole) in a 250-milliliter (mL) beaker was dissolved in 50 mL of distilled water. To this was added 11.5 mL of 70% HNO₃, by drops, while stirring. A white precipitate crashed out of solution immediately. Upon completion of the HNO₃ addition, the mixture was allowed to stir at 25 °C for 15 min, after which, it was filtered and washed with 15 mL of cold water. A total amount of 7.0 g of wet material was recovered from the initial acid treatment. The mother liquor was then cooled to 0 °C with an ice bath and an additional 11.5 mL of 70% HNO₃ was added by drops. A luminous white precipitate formed immediately. Upon completion of the addition, the mixture was filtered, the filter cake washed with 15 mL of ice-cold water and both filtrates were combined. The white powder was dried in a vacuum oven at 50 °C and 10 torr for 5 h, after which 24.5 g of a white powder melting with decomposition at 160 °C was recovered. The dried product was stored under vacuum in a desiccator equipped with fresh drierite.

4.3 Sensitivity Testing

The sample of UN was subjected to a battery of sensitivity tests including impact, friction, and electrostatic discharge. The impact testing was conducted according to the Langley one-shot method which reports the sensitivity as an average height at which 50% of the samples result in decomposition (H₅₀). Using this method, the sample was found to have an H₅₀ value of >61 inches. A 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) standard analyzed on the same day yielded an H₅₀ value of 10.054 ± 0.620 inches.

5. Conclusions

From the results of the thermal analysis study, it can be concluded that urea nitrate is thermally stable if stored below 60 °C. While it was known that UN exhibits mass loss at elevated temperatures, very little work has been previously done regarding how to safely store the material at more reasonable temperatures. From the plot shown in Fig. 2, it is apparent there is roughly tripling in the rate of mass loss of the material when it is exposed to temperatures above 60 °C and that rate of mass loss again quadruples when the temperature rises above

80 °C. However, in all cases, the material had only lost at maximum 12% of its weight under all of the testing conditions at 500 min. Using the rate of mass loss, even at 90 °C it would take more than 3 days of continuous exposure to those conditions for UN to completely decompose. The rate of mass loss at elevated temperatures can be reduced through simply covering the samples. At 80 °C, a UN sample that had been covered in a pan with a pinhole lost approximately 60% less mass than the uncovered sample with an almost 40% reduction in the rate of mass loss. From these results it can be concluded that UN is safe to store under normal energetic material storage conditions.

6. References and Notes

1. UN with a density of 1.2 g/mL in a 30-mm-diameter steel tube has a detonation velocity of 4700 m/s compared to ammonium nitrate with a density of 0.98 g/mL in an 80-mm steel tube having a detonation velocity of 2700 m/s.
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List of Symbols, Abbreviations, and Acronyms

[A]	concentration of UN
[A] ₀	concentration at time 0
DC	diamond cell
DSC	differential scanning calorimetry
g	gram
H ₅₀	height at which 50% of samples exhibit decomposition
HNO ₃	nitric acid
IR	infrared
<i>k</i>	rate constant
mL	milliliter
RDX	1,3,5-trinitroperhydro-1,3,5-triazine
<i>t</i> _½	half-life
TGA	thermogravimetric analysis
UN	urea nitrate

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